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[54]发明名称 改进的电解制氟方法及专用的电解槽

[57]摘要

一种改进的电解制氟方法及新颖的电解槽。该电解槽中的阴极被设计成换热部件,并且是唯一的换热部件。阴极与槽体绝缘,也与输送载热流体的管道绝缘。采用不导电的热稳定性流体作载热流体。不存在换热器被腐蚀穿孔的危险,也不存在氢气与氟气混合的危险,同时不存在电流通过槽体或载热流体输送管道或通过载热流体本身所引起的电能的无益消耗。这种电解槽结构简单,操作方便,可以根据不同要求的单槽生产能力,用数目不同的阴极换热部件组合成各种规格的电解槽。

权 利 要 求 书

1、一种电解制氟方法，使用熔融的由碱金属的氟化物与氟化氢组成的组合物作电解质，以碳质材料作阳极，以普通碳钢作阴极，其特征在于，使用一种具有特殊结构的电解槽，在该电解槽中，阴极同时起换热器的作用，阴极内部具有可让载热流体流过的通道，阴极与载热流体输送管道之间以及阴极与槽体之间皆进行电绝缘，使用一种不导电的热稳定性流体作载热体，在开始电解时，依靠在阴极内部通道流动的不导电流体所输入的热量使电解质熔化，在电解过程中依靠所说的载热流体把由于电解作用所产生的热量带走，使电解质的温度保持在正常的操作温度 $75^{\circ}\text{C}-150^{\circ}\text{C}$ 。

2、如权利要求1的电解制氟方法，其中所说的不导电的热稳定性载热流体是一种导热的液体。

3、如权利要求1或2的电解制氟方法，其中所说的不导电的热稳定性载热流体是一种导热油。

4、如权利要求3的电解制氟方法，其中所说的不导电的热稳定性载热流体是变压器油。

5、如权利要求1的电解制氟方法，其中所说的电解质温度为 $80^{\circ}\text{C}-130^{\circ}\text{C}$ 。

6、如权利要求1或5的电解制氟方法，其中所说的电解质温度为 $80-110^{\circ}\text{C}$ 。

7、如权利要求1或6的电解制氟方法，其中所说的电解质

温度为95—105℃。

8、一种用于实施权利要求1的电解制氟方法的电解槽，该电解槽采用碳质材料的阳极和普通碳钢的阴极，阳极和阴极之间有隔离裙将电解生成的氟与氢隔开，其特征在于，阴极(3)本身具有换热器的结构，其内部具有能允许载热流体经过的通道(4)，不存在与槽体(1)等电位的换热器，阴极(3)与槽体(1)之间有绝缘填料(11)隔开，阴极与载热流体输送管道之间有绝缘垫片或绝缘接管(12)隔开。

9、如权利要求8的电解槽，其中所说的阴极内部的载热流体通道呈夹套状。

10、如权利要求8的电解槽，其中所说的阴极内部的载热流体通道呈蛇形管状。

11、如权利要求8的电解槽，其中所说的阴极内部的载热流体通道呈列管状。

12、如权利要求8的电解槽，其中所说的阴极内部的载热流体通道对各阴极来说是并联的。

13、如权利要求8的电解槽，其中所说的阴极内部的载热流体通道对各阴极来说是串联的。

14、如权利要求8或12的电解槽，其中所说的阴极内部的载热流体通道是通过槽内进行并联的。

15、如权利要求8或12的电解槽，其中所说的阴极内部的

载热流体通道是通过槽外进行并联的。

16、如权利要求8或13的电解槽，其中所说的阴极内部的载热流体通道是通过槽内进行串联的。

17、如权利要求8或13的电解槽，其中所说的阴极内部的载热流体通道是通过槽外进行串联的。

改进的电解制氟方法及
专用的电解槽

本发明涉及一种改进的电解制氟方法及专门用于此方法的改进型电解槽。

氟在化工生产上有重要的用途，它可用于各种氟化工艺，尤其在原子能工业上被大量地用来生产 UF_6 。

通常，氟是在 $100^{\circ}C$ 左右，以熔融 $KF \cdot 2HF$ 为电解质，在一个以碳质电极为阳极，以钢板为阴极的电解槽中电解 HF 而制得的。

因为 $KF \cdot 2HF$ 的熔点为 $71.7^{\circ}C$ ，在常温下它呈固体状态，所以在电解槽启动时需要从外部供热以使电解质熔化。另一方面，在正常的电解过程中，为了使槽温保持在 $80-110^{\circ}C$ 的范围，必须把电解反应产生的热和由于电解质电阻放出的热及时带走，否则槽温将不断上升。因此在电解装置中必须设置一个热交换器并往其中通过一种载热流体，借此来实现电解质的加热和冷却。

在以往的方法中，通常用于制氟的电解槽均在槽体器壁的外面加一层夹套，以此作为换热器，以水蒸汽和水作为载热体，使该载热体通过所说的夹套流动，借此实现电解质的加热或冷却。

因为一般的水是导电体，并且其输送管道通常是接地的，在此情况下电解槽的换热部件也必然是接地的，因此，用水蒸汽和水作为载热体来实现热交换的电解槽换热部件通常是与槽体等电位的。

另外，在以往的方法中，通常采用下列两种类型的电解槽：

- 1、阴极与槽体电连接，隔离裙与槽体电绝缘；
- 2、阴极与槽体电绝缘，隔离裙与槽体电连接。

作为第一种类型的电解槽的例子有US3, 146, 179和US 3, 000, 801等。这类电解槽的槽体以及换热器由于与阴极电连接而得到电化学保护，因此换热器不易被腐蚀穿孔，所以也就不会引起载热体泄漏入电解槽中，但是由于槽体与阴极电连接，这样槽体就与阴极具有相等的电位，因此在电解过程中槽壁与槽底都会产生氢气。为了防止槽底产生的氢气进入阳极区域，必须在电解槽底面上覆盖以电绝缘物。另外，这类电解槽的隔离裙必须与槽体绝缘，这在结构上也是比较困难的。因此，这类电解槽的槽体结构以及电解操作都较为复杂。再有，由于阴极与接地的槽体和换热部件电连接，这样，阴极实际上就是接地的，因此造成了电能的额外消耗。所以这类电解槽在70年代以后已很少使用。

作为第二种类型电解槽的例子有US4, 139, 447和US4, 511,

440等，这类电解槽与第一种类型的电解槽相比，其优点是避免氢气混入氟气中的危险，而且由于阴极与接地的槽体和换热部件绝缘，因此避免了电能的额外消耗。但这类电解槽的最大缺点是槽体以及与其相连接的换热部件由于与阴极绝缘而得不到电化学保护，因此易于被电解质腐蚀，当换热器一旦被腐蚀穿孔，作为载热体的水就会立即漏入电解槽内，使电解质及碳阳极受到严重损害。虽然这两份专利文件都提到了可用蒙乃尔合金作为槽体与换热器的材料，以使它们具有耐腐蚀的性能，然而这就明显地增加了设备的造价。

本发明的目的是要提供一种能克服上述两类先有技术的缺点的电解制氟方法及专用于此方法中的改进型电解槽。也就是说，本发明将提供的电解制氟方法和专用的电解槽应该是既能有效地防止电解生成的氢气混入氟气中，保证生产的安全与产品的纯度，同时又能消除电能的额外消耗，降低生产成本，而且还能消除换热器被腐蚀穿孔以及由此而导致载热体漏入电解槽中的危险，并且该电解槽的结构简单，设备成本低，操作容易。

本发明人经过深入的研究，总结出下述的几点技术方案：

- 1、将阴极设计成换热部件，也就是在阴极内部存在允许载热流体通过的通道，同时取消了与槽体等电位的换热部件；
- 2、用绝缘材料使阴极既与槽体绝缘，同时也与载热流体

的输送管道绝缘；

3、在电解工艺方法上基本上仍采用常规的工艺条件，包括使用同样的电解质、操作温度和电流密度。所不同的是本发明的方法采用了上述的改进型电解槽，并且选用了一种不导电的流体作为载热体。

正如上述，由于阴极与槽体绝缘，因此除了阴极以外，槽体的任何部件皆不会产生氢气，所以不存在氢气与氟气相混的危险。另外由于阴极与载热流体输送管道绝缘，并且采用了不导电的载热流体，因此不存在电流通过槽体或载热流体输送管道或通过载热流体本身所引起的电能的无益消耗。再有就是由于取消了与槽体等电位的换热部件而将阴极本身设计成换热部件，因此使换热部件获得了电化学保护，所以不存在换热部件被腐蚀穿孔并由此而引起的载热流体漏入电解质中的危险。并且这样的电解槽结构简单，阴极和槽体皆可以用普通碳钢制造，设备造价低廉，而且操作方便。由于研究出了这种有效的电解制氟方法和这种具有新颖结构的改进型电解槽，至此就完成了本发明。

实际上，本发明的电解制氟方法及专用的电解槽所具有的优点来自其新颖的构思，而它们对工艺的操作条件和设备的制造都没有很严格的要求。下面将对本发明的特征作较详细的叙述。

在本发明的方法中使用的电解质为一般的制氟用电解质，它通常由碱金属的氟化物与氟化氢组成，较常用的是由KF和HF组成，其摩尔比例通常可以为 $\text{KF}:\text{HF}=1:1.8-1:2.2$ (摩尔)，最常用的为 $1:2$ (摩尔)，也就是一种组成约为 $\text{KF}\cdot 2\text{HF}$ 的电解质。电解温度没有严格的限制，只要能保证电解质处于熔融状态即可，例如通常应至少高于 75°C ，另一方面，温度太高也会给电解工艺带来不利的影响，但是由于本发明所用电解装置中的换热器就是阴极本身，它获得很好的电化学保护，故不存在被腐蚀穿孔的危险，因此在本发明的方法中，电解温度的上限可以明显地高于已知方法中的温度上限。对于本发明的方法来说，电解温度适宜在 $75-150^{\circ}\text{C}$ 之间，但通常较多地采用 $80-130^{\circ}\text{C}$ ，较佳地为 $80-110^{\circ}\text{C}$ ，而最好为 $95-105^{\circ}\text{C}$ ，即在 100°C 左右。

本发明的方法中使用的不导电载热流体没有严格的限制，只要它具有热稳定性，同时既不导电又能起热交换的作用即可。它可以是气体，也可以是液体。其中适用气体的例子有：空气、氮气、二氧化碳等对热稳定的不导电气体，但其中以空气较为方便。适用的液体通常是不含水分的各种油类，其例子有：煤油、柴油、液体石蜡、石油副产品中的各种液态烃类混合物、各种牌号的导热油，其中包括变压器油。在上述各类油中，以导热油为较佳。

本发明的电解槽的最重要的特征之一是，阴极本身作为换

热部件并且是该电解装置中唯一的换热部件，也就是阴极内部必须具有可让载热流体流过的通道，但对于通道的形式没有严格的限制，只要它能起换热的作用即可。例如，较适宜的通道可以是：夹套、蛇形管、列管等。这些通道在各阴极之间可以按不同的方式连接，既可以并联，也可以串联。对于不同的连接方式，既可以通过槽内实现，也可以通过槽外实现。

阴极与载热体导管绝缘也是本发明的重要特征之一，它可以采用任何方式绝缘，例如可以采用绝缘垫片，也可以用一段由绝缘材料制成的管。

上面已对本发明的技术方案及其特征作了详细说明，正是由于这些新颖的技术方案使得本发明的电解制氟方法和专用于该方法的电解槽具有如下的有益效果：

- 1、由于阴极本身是唯一的换热部件，因此不存在换热部件被腐蚀穿孔的危险，可以使用较宽范围的电解温度，生产过程安全而稳定，设备的使用寿命长；
- 2、除阴极以外，电解槽其他各部分皆没有氢气产生，因此不存在氢气与氟气混合的危险，产品的纯度高；
- 3、设备的结构及其操作方法都很简单；
- 4、由于采用不导电的载热流体和实现阴极与载热流体的输送管道之间的电绝缘，因此不会造成电能的无益消耗；
- 5、设备投资和生产费用都比较低廉。

图3是本发明电解槽的平剖面示意图，

其中: 1…槽体; 2…碳阳极; 3…阴极兼换热部件; 4…载热流体通道; 5…隔离裙; 6… F_2 出口; 7… H_2 出口; 8…阴极导电管; 9…阳极导电杆; 10…电解槽盖; 11…绝缘填料; 12…绝缘垫片或绝缘接管; 13…电解质液面; 14…载热流体通道连通管; 15…HF通入口。

下面结合实施例对本发明作进一步的解释，但应说明，这些实施例只是实施本发明的较佳方式之一，它对本发明的范围不起限定作用。本领域的普通技术人员只需根据本发明的实质性特点，即能作出各种不同的变化和修改，但应理解，只要具有本发明的实质性特点，则所有的各种变化皆应被视为属于本发明的范围。

实施例1

设备 1500A电解槽

设备各部件的材质和载热流体的种类:

槽体 碳钢

隔离裙 碳钢

阴极	碳钢
阳极	无定形碳
载热流体	导热油 (牌号BR280)
槽体尺寸	220×90×45cm
每块阳极尺寸	63×18×5cm
阳极组数	2组
阳极板总数	16块 (每组8块)
阴极板尺寸	170×45×3cm
阴极板块数	3块

(即在两组阳极的中间和左右两侧各有一块阴极板)

槽总电压	10V
电解质组成	KF : HF=1 : 2
电解试验时间	共3600小时
总加料量	HF 7100kg
产品F ₂ 总量	3490kg
相对于F ₂ 的电流效率	91%

设备腐蚀情况: 阴极无腐蚀现象, 槽体及隔离裙焊缝轻微腐蚀。

试验电解槽制作方便, 造价低, 电解槽生产稳定, 操作方便。槽内电解质各部位温度均匀, HF消耗低。即使槽体腐蚀穿孔, 只有少量电解质外漏, 只须停槽, 将电解质捞出, 槽体经修补后仍可继续用于生产, 当然, 若槽体和隔离裙用蒙乃尔合金制作, 效果将会更好。

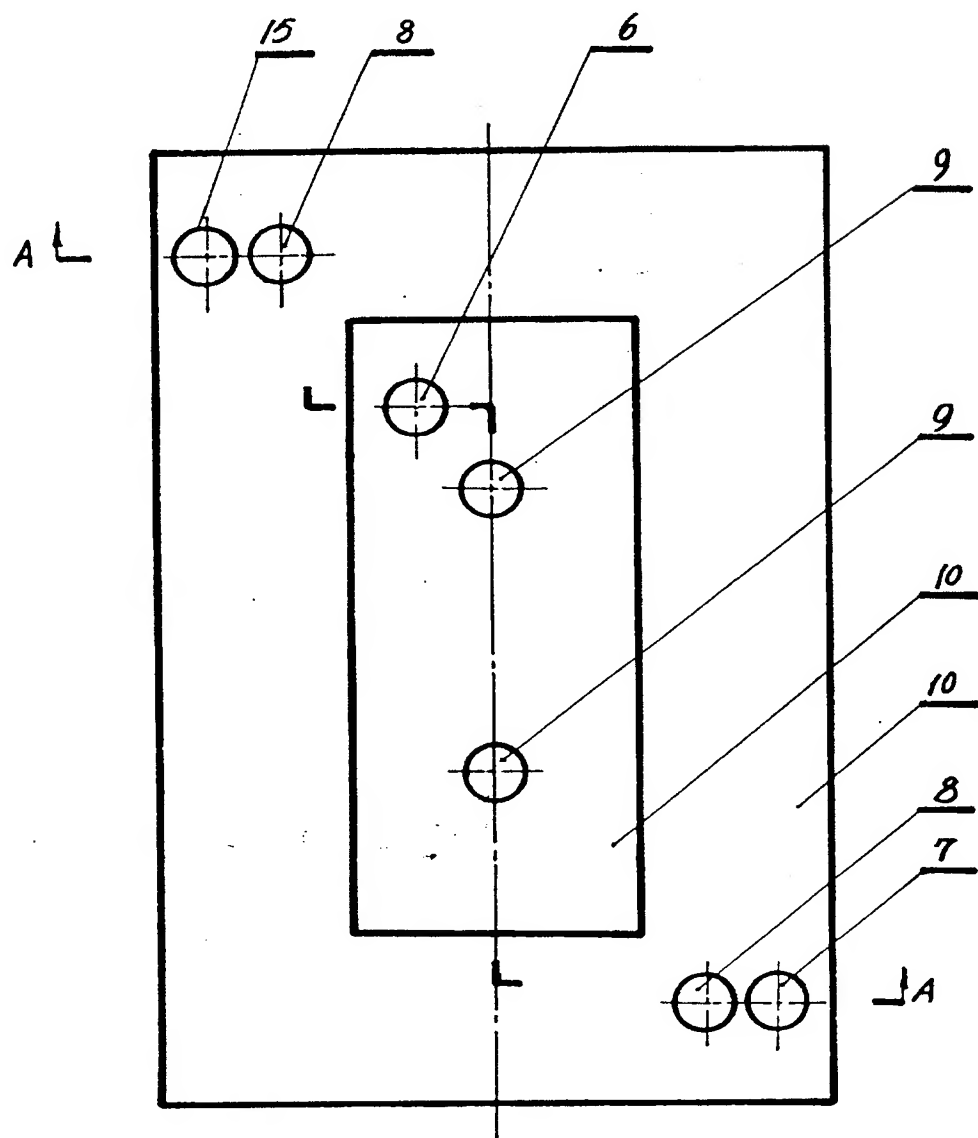


图1: 具有二组阳极的制氧电解槽

俯视示意图

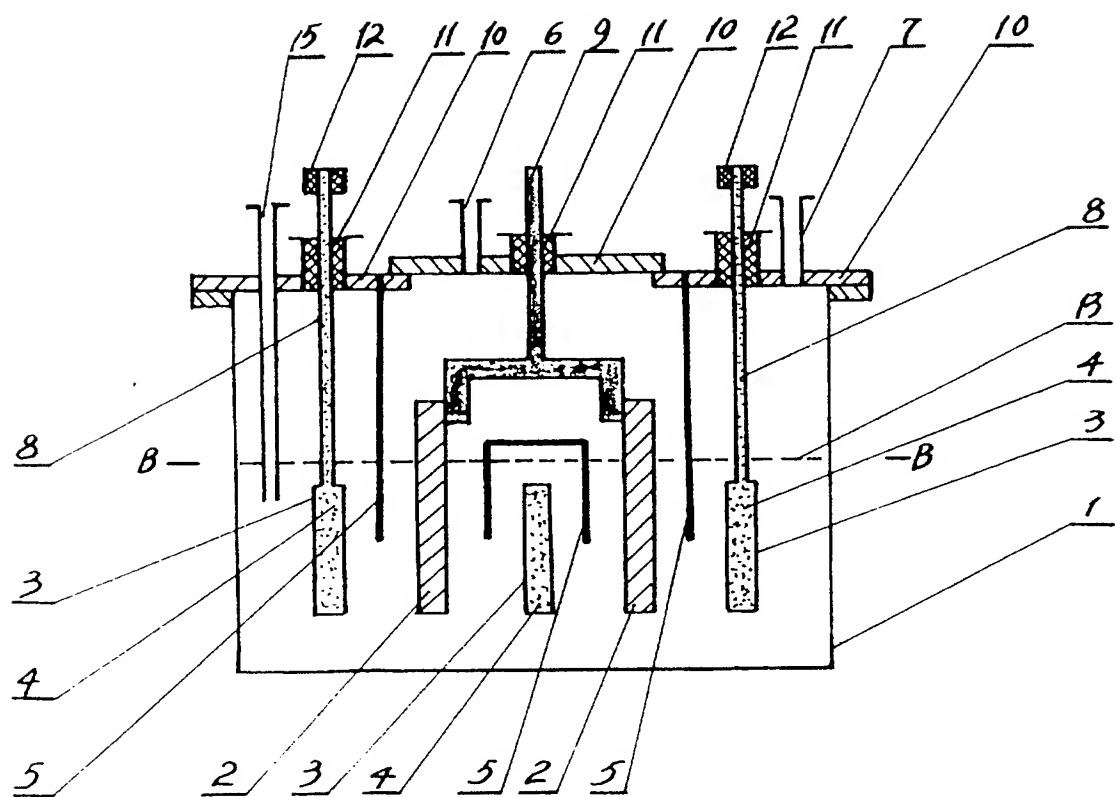


图2: 具有二组阳板的电解槽
A-A 剖面示意图

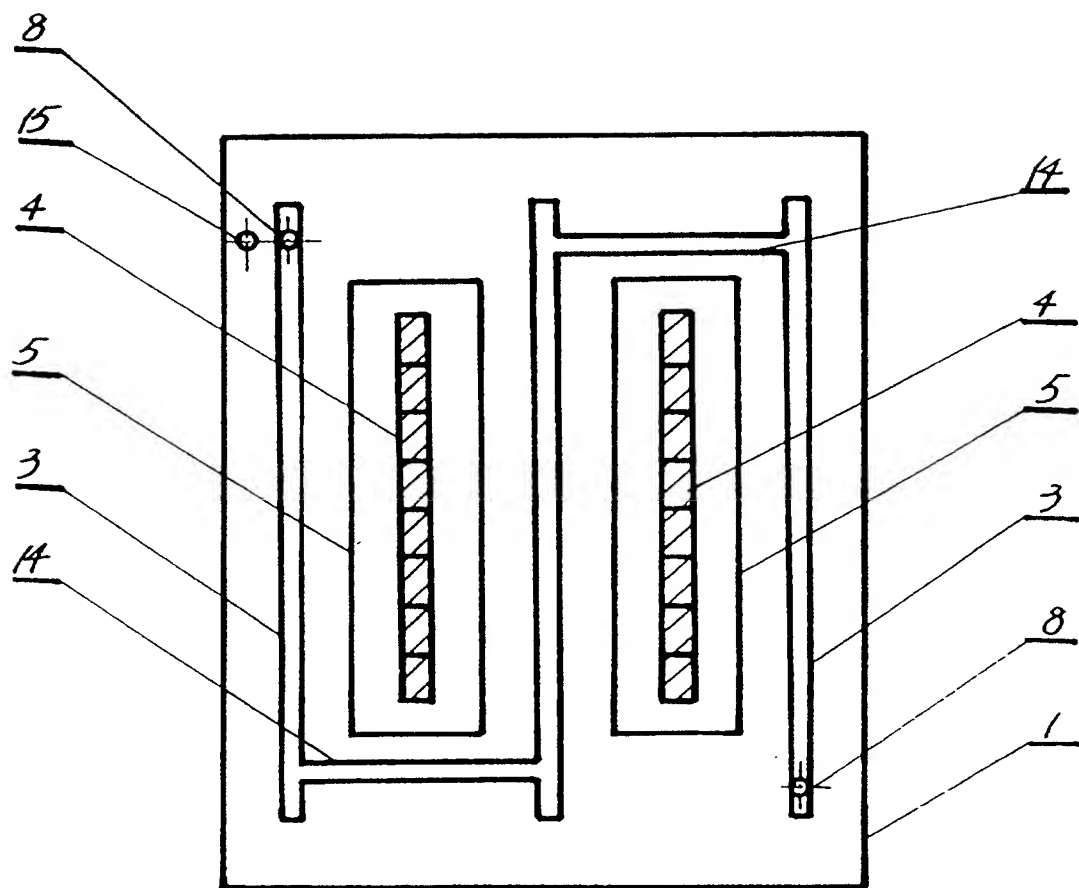


图3. 具有二组阳极的制氧电解槽

B-B 平剖面示意图

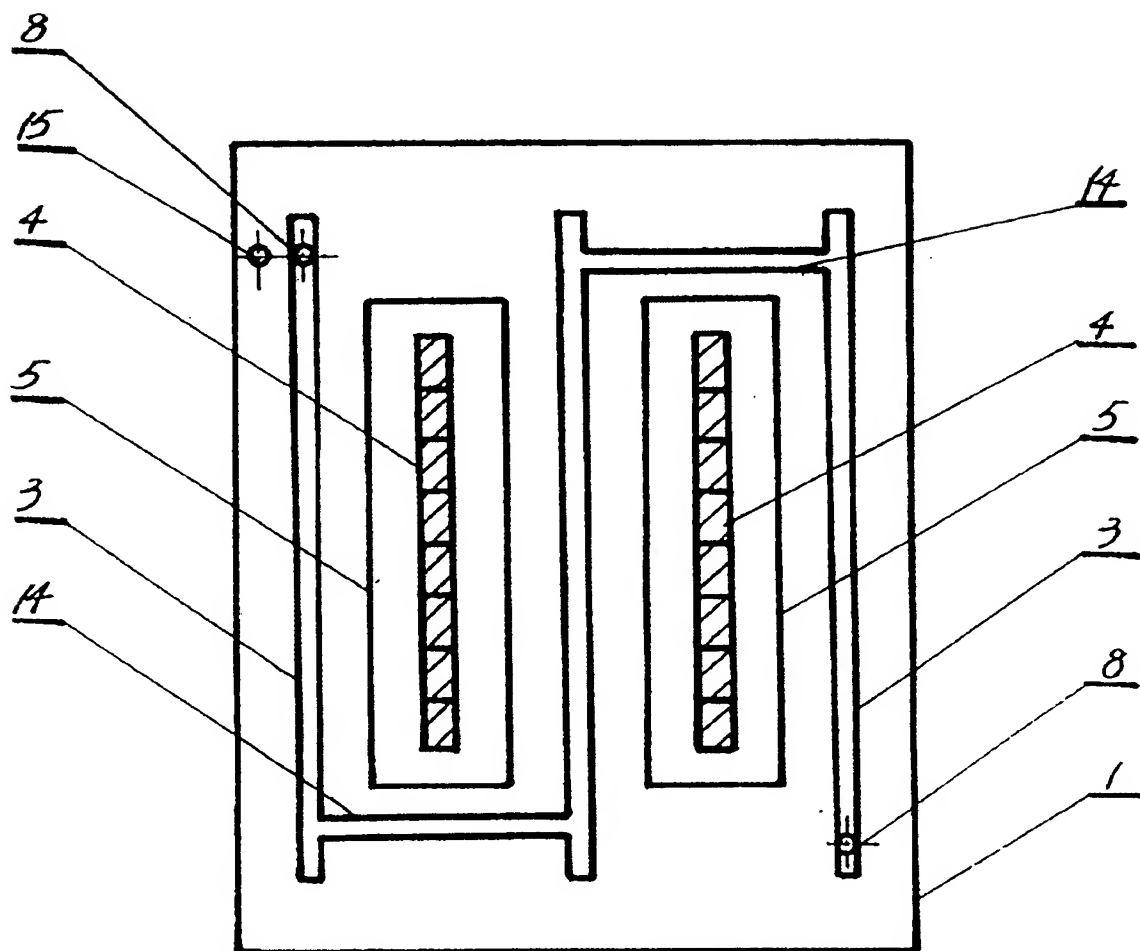


图3: 具有二组阳极的制氧电解槽

B-B 平剖面示意图

[54] Title of the Invention: IMPROVED ELECTROLYTIC FLUORINE
MANUFACTURING METHOD AND EXCLUSIVE ELECTROLYTIC CELL

[57] Abstract

One type of improved electrolytic fluorine manufacturing method and a novel electrolytic cell. A cathode inside the electrolytic cell is designed as a heat exchanger, and as only a heat exchanger. The cathode is insulated from a cell body, and also insulated from a pipe transporting thermal fluid. A thermally stable fluid without electrical conductivity is employed as a thermal fluid. The heat exchanger has no risk of being perforated by corrosion, and also no risk that hydrogen and fluorine mix together. At the same time, excess consumption of electrical energy, which is caused in such a way that electricity passes through the cell body or a thermal fluid transporting pipe, or that it is generated through the thermal fluid itself, does not exist. Since this type of electrolytic cell is simple in structure, and excellent in operation, based on a single cell production capacity different in requirement, variously regulated electrolytic cells can be composed by using cathode heat exchangers different in number.

What is claimed is:

1. One type of electrolytic fluorine manufacturing method of manufacturing fluorine, in which a compound consisting of a fluorine compound of a molten alkali metal and hydrogen fluoride is set to be an electrolyte, and a carbon material is set to be an anode, furthermore an ordinary carbon steel is set to be a cathode, comprising:

using an electrolytic cell preparing a special structure;

performing heat exchanging actions with the cathodes simultaneously inside the electrolytic cell;

preparing a passage passing through a thermal fluid inside the cathode;

performing electrical insulation entirely between the cathode and a thermal fluid transporting pipe, and between the cathode and a cell body;

using one type of thermally stable fluid without electrical conductivity as a thermal carrier;

melting the electrolyte by the quantity of heat flowed in by a fluid which flows inside a passage in the cathode, and has no electrical conductivity when starting electrolysis;

taking away the quantity of heat generated by the electrolytic action with the thermal fluid in an electrolytic process;

and keeping an electrolyte temperature between 75°C and 150°C, which is a normal operation temperature of the electrolyte.

2. An electrolytic fluorine manufacturing method according to claim 1, wherein a thermally stable thermal fluid without electrical conductivity is a liquid with thermal conductivity.

3. An electrolytic fluorine manufacturing method according to claim 1 or claim 2, wherein a thermally stable thermal fluid without electrical conductivity is one type of oil with thermal conductivity.

4. An electrolytic fluorine manufacturing method according to claim 3, wherein a thermally stable thermal fluid without electrical conductivity is a transformer oil.

5. An electrolytic fluorine manufacturing method according to claim 1, wherein an electrolyte temperature is between 80°C and 130°C.

6. An electrolytic fluorine manufacturing method according to claim 1 or claim 5, wherein an electrolyte temperature is between 80°C and 110°C.

7. An electrolytic fluorine manufacturing method according to claim 1 or claim 6, wherein an electrolyte temperature is between 95°C and 105°C.

8. One type of electrolytic cell used for processing an

electrolytic fluorine manufacturing method according to claim 1, wherein:

the electrolytic cell employs an anode made of a carbon material and a cathode made of plain carbon steel; wherein there is a diaphragm, which separates fluorine and hydrogen generated in electrolysis, between the anode and the cathode; wherein the cathode (3) itself prepares a structure of the heat exchanger; wherein a passage (4) capable of passing through the thermal fluid is provided inside the cell; wherein a heat exchanger equivalent to the cell body (1) in potential does not exist; wherein the cathode (3) and the cell body (1) are separated by an insulating filler (11); and wherein the cathode and the thermal fluid transporting pipe are separated by an insulating spacer or an insulating attaching pipe (12).

9. An electrolytic cell according to claim 8, wherein a thermal fluid passage in the cathode exhibits a folding-shaped profile.

10. An electrolytic cell according to claim 8, wherein a thermal fluid passage in the cathode exhibits a serpentine pipe profile.

11. An electrolytic cell according to claim 8, wherein a thermal fluid passage in the cathode exhibits a row-shaped pipe profile.

12. An electrolytic cell according to claim 8, wherein a thermal fluid passage in the cathode stands in parallel with respect to each cathode.

13. An electrolytic cell according to claim 8, wherein a thermal fluid passage in the cathode stands in series with respect to each cathode.

14. An electrolytic cell according to claim 8 or claim 12, wherein thermal fluid passages in the cathode pass inside the cell and stand in parallel.

15. An electrolytic cell according to claim 8 or claim 12, wherein thermal fluid passages in the cathode pass outside the cell and stand in parallel.

16. An electrolytic cell according to claim 8 or claim 13, wherein thermal fluid passages in the cathode pass inside the cell and stand in series.

17. An electrolytic cell according to claim 8 or claim 13, wherein thermal fluid passages in the cathode pass outside the cell and stand in series.

Specification

IMPROVED ELECTROLYTIC FLUORINE MANUFACTURING METHOD AND EXCLUSIVE ELECTROLYTIC CELL

The present invention relates to one type of improved fluorine manufacturing method and an improved type electrolytic cell exclusive to this method.

Fluorine has an important application in chemical industry production, and can be used for various fluorination technologies, in particular, is used frequently for production of UF₆ throughout the nuclear industry.

In general, fluorine is manufactured at 100°C or so inside an electrolytic cell in such a way that a molten KF-2HF is set to be an electrolyte, that a carbon electrode is set to be an anode, and that a steel plate is set to be a cathode.

Since the KF-2HF has a melting point of 71.7°C, and exhibits solid state under normal temperature, it is necessary for the KF-2HF to melt the electrolyte by supplying heat from the outside when starting electrolytic cell operation. On the other hand, in a normal electrolytic process, for keeping a temperature of the electrolytic cell in a range between 80°C and 110°C, heat generated by electrolytic reaction and heat radiated by a

resistance of the electrolyte are required to be removed quickly, otherwise, the temperature of the electrolytic cell increases constantly. Therefore, a heat exchanger is required to be arranged inside an electrolytic apparatus, and one type of thermal fluid is necessary to pass within the apparatus, and heating/cooling the electrolyte is realized through the fluid.

In conventional methods, heating/cooling the electrolyte was realized in such a way that the electrolytic cell used for manufacturing fluorine, normally, was equipped with a double covering on an external surface of cell walls of the cell body in all cases, that they were set to be a heat exchanger, that steam and water were used as thermal carriers, and that these thermal carriers were passed through the double covering.

Normal water is an electrical conductor, and since the transporting pipe is normally earthed, the heat exchanger of the electrolytic cell under this condition is also necessarily earthed. Accordingly, the heat exchanger of the electrolytic cell which realizes heat exchange using steam and water as the thermal carriers is normally equivalent in potential to the cell body.

Except for the above, in the conventional methods, the following two types of electrolytic cells are usually employed.

1. The cathode is conductive with respect to the cell

body, and a diaphragm is electrically insulated with respect to the cell body.

2. The cathode is electrically insulated with respect to the cell body, and the diaphragm is conductive with respect to the cell body.

As one example of a first type of electrolytic cell, there is US3, 146, 179 or US3, 000, 801 or the like. Since the cell body of this type of electrolytic cell and the heat exchanger are conductive with respect to the cathode, they can acquire electrolytic protection; therefore, it is difficult for the heat exchanger to be perforated by corrosion, and the thermal carrier has no opportunity to cause leakage into the electrolytic cell. However, since the cell body is conductive with respect to the cathode, the cell body like this is equivalent in potential to the cathode, therefore, hydrogen is generated from both the cell walls and cell bottom in the electrolytic process. In order to prevent the hydrogen occurring in the cell bottom from invading into an anode region, it is necessary to cover an electrolytic bottom surface with an electrical insulator. In addition, with this type of electrolytic cell, it is necessary to insulate the diaphragm from the cell body, which is relatively difficult to achieve structurally. Accordingly, both a cell structure of the electrolytic cell of this type and an

electrolytic operation become relatively complicated. Furthermore, the cathode is conductive with respect to the cell body or the heat exchanger which is earthed, as a result, the cathode is in actuality earthed, therefore, excess consumption of electrical energy is caused. Accordingly, use of this type of electrolytic cell has become less since the 1970s.

As an example of a second type of electrolytic cell, there is US4, 139, 447 or US4, 511, 440 or the like. This type of electrolytic cell has, compared with the first type of electrolytic cell, an advantage of avoiding the risk of mixing hydrogen with fluorine, moreover, since the cathode is insulated with respect to the cell body or the heat exchanger which is earthed, excess consumption of electrical energy can be avoided. However, the greatest defect with this type of electrolytic cell is that the electrolytic protection cannot be obtained because the cell body and the heat exchanger connected to the cell are insulated with respect to the cathode, therefore, they easily corrode by electrolytes, and when the heat exchanger is perforated by corrosion once, water as the thermal carrier leaks into the electrolytic cell immediately, and the electrolyte and a carbon anode are damaged in extremity. These two patent documents disclose that they can be equipped with anti-corrosion capability by employing monel metal as a material

of the cell body and the heat exchanger, however, this makes the construction cost of equipment clearly increase.

The purpose of the present invention is to provide one type of electrolytic fluorine manufacturing method and an improved type electrolytic cell used exclusively for this method which can overcome the defects of prior arts of both types mentioned above. That is, the electrolytic fluorine manufacturing method and the exclusive electrolytic cell which are provided by the present invention effectively prevent the hydrogen generated by the electrolysis from mixing with the fluorine, and safety in production and purity of product can be thereby guaranteed, while production costs can be reduced by eliminating excessive consumption of electrical energy simultaneously, moreover, the heat exchanger is prevented from being perforated by corrosion and a resulting risk, of making the thermal carrier leak into the electrolytic cell is eliminated. Furthermore, the electrolytic cell is simplified in structure, low in equipment cost, and easy in operation.

The inventor of the present invention summarized the present invention into the following several technical methods through in-depth research.

1. Design is processed by fixing the cathode to be the heat exchanger, that is, a passage permitting the thermal fluid

to pass inside the cathode exists, and the heat exchanger equivalent in potential to the cell body is eliminated simultaneously.

2. The cell body and the cathode are made to be insulated from each other using an insulating material, and to be insulated from a transporting pipe of the thermal fluid simultaneously.

3. On a method of electrolytic technology, basically, an ordinary technical condition including the same electrolyte, operation temperature and current density is employed. In another aspect, the method of the present invention employs the above-mentioned improved type electrolytic cell, and selects one type of fluid without electrical conductivity as a thermal carrier.

As mentioned above, the cathode is insulated from the cell body, therefore, since any portion of the cell body except the cathode will not generate hydrogen, the hydrogen and the fluorine have no risk of being mixed together. In addition, since the cathode is insulated from the transporting pipe of the thermal fluid, and thermal fluid without electrical conductivity is employed, excessive consumption of electrical energy, which is caused in such a way that the current flows through the cell body or the thermal fluid transporting pipe, or that it is caused by the thermal fluid itself, does not exist.

Furthermore, the heat exchanger can be protected by the electrolytic protection by designing the cathode itself to be a heat exchanger by eliminating the heat exchanger equivalent to the cell body in potential, accordingly, the heat exchanger has no risk of being perforated by corrosion, and no resulting risk which may cause the thermal fluid to leak into the electrolyte exists. Moreover, since the electrolytic cell like this is simple in structure, and the cathode and cell body can be constructed using plain carbon steel, equipment construction is low in cost, and operation is convenient. The present invention has been completed in such a way that this type of effective electrolytic fluorine manufacturing method and the improved electrolytic cell equipped with this type of novel structure are studied and developed.

In actuality, an advantage prepared by the electrolytic fluorine manufacturing method and the exclusive electrolytic cell of the present invention is derived from its novel concept, and there is no strict requirement on operating conditions or equipment construction with respect to those technologies. Next, characteristics of the present invention are described in a relatively detailed manner.

The electrolyte used for the present invention is a typical electrolyte used for manufacturing fluorine, and consists of

a fluorine compound of alkali metal and a hydrogen fluoride, and of KF and HF of relatively common use. Its mole ratio is $\text{KF}:\text{HF}=1:1.8$ to $1:2.2$ (mole) normally, and the most commonly used one is $1:2$ (mole), and is an electrolyte with a composition ratio of $\text{KF}\cdot 2\text{HF}$ in roughness. The electrolytic temperature is not strictly limited, and it is satisfactory if only a molten condition of the electrolyte can be guaranteed. For example, normally, its temperature will be more than at least 75°C , on the other hand, excessively high temperature causes the electrolytic technology to accept a "minus" influence. However, the heat exchanger in the electrolytic apparatus used for the present invention is the cathode itself, and since it is equipped with an excellent electrolytic protection, it has no risk of being perforated by corrosion. Therefore, in the method of the present invention, an upper limit of the electrolytic temperature is permitted to be higher than that of a temperature in a conventional method. A suitable electrolytic temperature of the method of the present invention is between 75°C and 150°C . However, normally, 80°C to 130°C is often employed, and 80°C to 110°C is relatively preferable, furthermore, 95°C to 105°C , that is, 100°C or so is the most suitable.

The thermal fluid without electrical conductivity which is used for the method of the present invention has no strict

limitation, and it is satisfactory if the thermal fluid is thermally stable, and simultaneously it bears a performance of heat exchange without performing electrical conductivity. It may be a gas or liquid. Among them, although as an example of an applied gas, there are gases such as air, nitrogen, carbon dioxide or the like which are stable with respect to heat and has no electrical conductivity, among them, air is relatively convenient. As an applied liquid, although there are various oils including no water normally, as an example, there is kerosene, diesel oil, liquid paraffin, various liquid hydrocarbon mixtures in petroleum byproducts or oils with thermal conductivity of various brands including transformer oil. Among the various types of oils mentioned above, oil with thermal conductivity is relatively preferable.

One of the most important characteristics of the electrolytic cell of the present invention is that the cathode itself constitutes the heat exchanger, and it is the only heat exchanger in the electrolytic apparatus. That is, although it is necessary to provide a passage capable of flowing the thermal fluid inside the cathode, the passage has no strict limitation in type. It is satisfactory if it can only perform heat exchanging. For example, as a relatively suitable passage, there is a folding-shaped, a serpentine pipe, row-shaped pipe or the like.

These passages can be connected between each cathode in a different method, and may be connected in parallel or in serial. Different connection methods can be made available regardless of whether they pass inside or outside the cell.

The cathode insulated from a thermal carrier conduit pipe is one of the most important characteristics of the present invention. They can employ any insulating method. For example, an insulating spacer can be used, and a pipe made of an insulating material is also available.

The technical method and its characteristics of the present invention are explained in detail above. And, these novel technical methods make the electrolytic fluorine manufacturing method of the present invention and the exclusive electrolytic cell used for the method equipped with advantageous effects mentioned below.

1. Since the cathode itself is the only heat exchanger, the heat exchanger has no risk of being perforated by corrosion, and an electrolytic temperature of relatively wide range can be employed, furthermore, the production process becomes safe and stable, therefore, equipment use life is extended.

2. Except for the cathode, the electrolytic cell and other portions generate no hydrogen. Therefore, there is no risk of mixing the hydrogen and the fluorine together, and its product

is high in purity.

3. The equipment is simple in both structure and operating method.

4. Since the thermal fluid without electrical conductivity is employed and insulation between the cathode and the transporting pipe of the thermal fluid is realized, no excessive consumption of electrical energy can be caused.

5. Both equipment investment and production cost are relatively low.

Next, attached drawings are explained briefly.

FIG. 1 is a schematic illustration of the electrolytic cell of the present invention viewed from top.

FIG. 2 is a longitudinal sectional view of the electrolytic cell of the present invention.

FIG. 3 is a transverse sectional view of the electrolytic cell of the present invention.

In the drawings: 1...cell body; 2...carbon anode; 3...cathode and heat exchanger; 4...thermal fluid passage; 5...diaphragm; 6...F₂ outlet; 7...H₂ outlet; 8...cathode conductive tube; 9...anode conductive rod; 10...electrolytic cell lid; 11...insulation filler; 12...insulating spacer or insulation attaching pipe; 13...electrolyte level; 14...thermal fluid passage connection pipe; 15...HF poring aperture

Next, the present invention is further explained by relating to the embodiment. However, it is clear that this embodiment is only one of the relatively preferable methods of the present invention, and there is no limitation with respect to the scope of the present invention. Any skilled technician in the present field can create various variations and modifications only based on the practical features of the present invention, however, the following matters shall be understood. That is, anything equipped with practical characteristics of the present invention including any various variations shall belong to the scope of the present invention.

Embodiment 1

Equipment	1500A electrolytic cell
Materials of each portion of the equipment and types of thermal fluid:	
Cell body	Carbon steel
Diaphragm	Carbon steel
Cathode	Carbon steel
Anode	Amorphous carbon
Thermal fluid	Oil with thermal conductivity (brand number: BR280)
Cell body size	220×90×45 cm

Size of 1 piece of the anode	63×18×5 cm
The number of set of the anode	2 sets
Total number of the anode	16 pieces (8 pieces in 1 set)
Cathode plate size	170×45×3 cm
The number of cathode plate	3 pieces
(That is, each 1 piece of cathode plate at a middle portion and both right and left sides of 2 sets of anodes)	
Cell total voltage	10V
Electrolyte composition	KF:HF=1:2
Electrolysis test time	Total 3600 hours
Material total poring quantity	HF 7100 kg
Product F ₂ total quantity	3490 kg
Relative current efficiency with respect to F ₂	91%

Corrosion state of the equipment: The cathode has no corrosion phenomenon, and the cell body and welding connection of the diaphragm have slight corrosion.

The test electrolytic cell is convenient in manufacturing, and is low in construction cost, furthermore, the electrolytic cell is stable in production, and convenient in operation. And, the electrolyte of each portion in the cell is uniform in temperature, and HF is low in consumption. Even when the cell body is perforated by corrosion, only a slight amount of electrolyte leaks out, and although the electrolytic cell has

to be halted in operation, it can be used continuously for production if the cell body is repaired after extracting the electrolyte. As a matter of course, when the cell body and the diaphragm are made of monel metal, its effect can be further expected.

Drawings Attached to Specification

FIG. 1: fluorine manufacturing electrolytic cell equipped with
2 sets of anodes

Schematic illustration viewed from top

FIG. 2: fluorine manufacturing electrolytic cell equipped with
2 sets of anodes

Sectional schematic illustration longitudinally sectioned by
the arrow A-A

FIG. 3: fluorine manufacturing electrolytic cell equipped with
2 sets of anodes

Sectional schematic illustration transversely sectioned by the
arrow B-B

FIG. 3: fluorine manufacturing electrolytic cell equipped with
2 sets of anodes

Sectional schematic illustration transversely sectioned by the
arrow B-B